

# Effects of gas hydrates on the chemical and physical properties of seawater

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## Abstract

Huge deposits of oceanic methane hydrate (MH) exist on the seafloor on continental margins. MH transforms into water and methane ( $\text{CH}_4$ ) gas in bubbles when it dissociates in seawater. That  $\text{CH}_4$  may be oxidized (via bacteria) into carbon dioxide ( $\text{CO}_2$ ) before the bubbles rise to the sea surface or dissolve into seawater again. Similarly, nitrogen hydrate is expected to exist in seawater. The nitrogen coming out of nitrogen hydrate can be fixed and oxidized into nitrate. Analysis of the relationship among seawater temperature, “apparent oxygen utilization” (AOU) and the concentration of  $\text{CO}_2$ , based on WOCE ocean observations, reveals some characteristics that are not part of a stoichiometry relation. Analysis of individual profiles implies that the dissociation of gas hydrates occurs according to temperature and pressure (depth) at hydrate phase boundary. A quantity, named as virtual oxygen utilization (VOU), is calculated to account for the depletion of dissolved oxygen in seawater due to biochemical oxidation processes. The results show a good agreement between AOU and VOU at depth greater than the level where hydrates dissociate. The VOU is less than AOU in the layer of seawater beneath the euphotic zone. That is attributed to the escape of  $\text{CO}_2$  into the atmosphere.

The oceanic MH provides a huge biochemical fuel source to generate heat internal to world oceans. This may explain the observed ocean warming at the intermediate depth during last several decades. The role of microbes in altering the chemical and physical properties of seawater and the course of climate change cannot be ignored.

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## 1. Introduction

Ocean exploration during last two decades indicates that huge deposits of oceanic methane hydrate (MH) exist on the seafloor on continental margins. MH transforms into water and methane ( $\text{CH}_4$ ) gas when it dissociates. Evidences indicate that a great population of tiny bubbles flows with ocean currents at intermediate depth before they rise to sea surface. This provides the

time for microbes (methane oxidation bacteria) to consume the  $\text{CH}_4$ . Earlier observations of  $\text{CH}_4$  bubbles in swamp and those generated from hydrothermal vents indicate that a great portion of  $\text{CH}_4$  has been oxidized (Reeburgh et al., 1993) before the bubbles finally rise to water surface or dissolve into seawater again.

Laboratory experiments demonstrate the existence of various gas hydrates (Sloan, 1998). Gases like  $\text{CO}_2$ , ethane, nitrogen, oxygen, etc., can also form hydrates within the temperature and pressure ranges of natural environments. Since seawater dissolves many gas species with significant concentration, one expects to find other gas hydrates besides MH in seawater. However, there is

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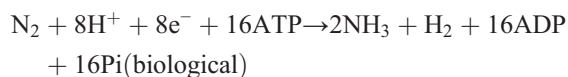
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no report regarding their abundance. This paper presents strong biochemical evidence of the abundance of other naturally-formed gas hydrates and their effects on the chemical and physical properties of seawater.

## 2. Data and methods

The data used in this research are extracted from the archives of observations in the World Ocean Circulation Experiment (WOCE, 1988–1998). All parameters (variables) available have been reviewed. But, the focus is analysis of vertical profiles of seawater temperature, concentrations of nitrate, CO<sub>2</sub> (hereafter, [nitrate] and [CO<sub>2</sub>], respectively) and oxygen using their “parameter vs. parameter” scatter plots. Temperature and [nitrate] in seawater have been measured, analyzed (and recorded) at most of stations along most of cruises in WOCE. Nitrate is an important and stable biochemical species in ocean nitrogen cycle. It is produced through the following processes (Stenes, 1998):

Nitrogen fixation;

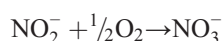


Nitrification;

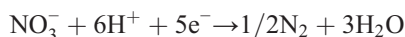
Step 1 Ammonia oxidation:



Step 2 Nitrite oxidation:



De-nitrification;



where ATP, ADP and Pi are Adenosine 5'-diphosphate, Adenosine 5'-triphosphate and inorganic phosphate, respectively. In the 2-step nitrification process, 2 moles of oxygen are used to oxidize 1 mole of ammonia into 1 mole of nitrate.

The dissolved CO<sub>2</sub> in seawater has two inorganic sources. One is the uptake of CO<sub>2</sub> gas from the atmosphere. The influx of CO<sub>2</sub> is a function of atmospheric CO<sub>2</sub> concentration and the sea surface temperature. The other is the dissolution of calcium carbonate. The concentration of calcium, [Ca<sup>2+</sup>], in seawater is almost a constant. However, the dissociation constant is a function of seawater temperature. Therefore, the concentration of CO<sub>3</sub><sup>2-</sup> in seawater is a function of temperature.

Photosynthesis in the euphotic zone in seawater utilizes CO<sub>2</sub> to build organic tissues and feeds the food chain. Finally, the dead tissues are disintegrated into CH<sub>4</sub>. But, some CH<sub>4</sub> can also be produced by methanogens through the sulfate reduction of CO<sub>2</sub>.

MH had been found on sea floor or beneath the ocean sediments. However, there are also observations of MH floating in seawater since the density of MH is slightly less than that of seawater. Eventually the MH will dissociate into water and CH<sub>4</sub>. Various methanotrophs take CH<sub>4</sub> as nutrient and oxidize it into CO<sub>2</sub>. In 1997, the discovery of methane ice worms (*Hesiocaeca methanicola*) (Fisher et al., 2000) living in the burrow on the surface of MH mound on sea floor indicated that some methanotrophs can utilize the CH<sub>4</sub> within MH before its dissociation and they might be the food for the methane ice worm.

The solubility of CH<sub>4</sub> in seawater is much smaller than that of CO<sub>2</sub>. The solubility of both gases decreases with temperature. After MH dissociates, part of the CH<sub>4</sub> within the bubble might get oxidized into CO<sub>2</sub>. Part of it will get into the atmosphere. To oxidize 1 mole of CH<sub>4</sub> into 1 mole of CO<sub>2</sub> consumes 2 moles of oxygen. Thus, the oxidation of CH<sub>4</sub> causes a significant depletion of dissolved oxygen in seawater near (and above) MH dissociation level. We call the difference between the saturated oxygen concentration (which is a function of temperature and salinity) and the measured oxygen concentration in seawater the “apparent oxygen utilization” (AOU).

Even though not all WOCE cruises took CO<sub>2</sub> measurement, there are enough data to reveal the general relationship between various parameters and CO<sub>2</sub>. The CO<sub>2</sub> data are derived from the values of “total carbon dioxide” (TCO<sub>2</sub>) and “total alkalinity” (TALK) (Dickson and Goyet, 1994). Both the TCO<sub>2</sub> and TALK are obtained from chemical analysis of bottles of seawater. Those analyses were performed in the research vessels and within specified time limits after sampling.

A computer program for ocean data-analysis, ODV (Schlitzer, 2004) has been used to generate figures for this paper. Fig. 1 presents the scatter patterns of AOU, [nitrate] and [CO<sub>2</sub>] (in panels (a)–(c)) of all stations along all WOCE cruise routes (shown in the map) that measured TCO<sub>2</sub> and TALK. All data points are color-coded with temperature data. Since there is a good relation between temperature and depth, these panels also present the relation between depth and the parameters shown.

Panel (a) of Fig. 1 shows a roughly constant ratio (slope of trail or the rate of change) between AOU and [nitrate] along a constant temperature surface. For example, the ratio is 10 along the 10 °C isotherm (the red line). This ratio decreases with temperature. On the

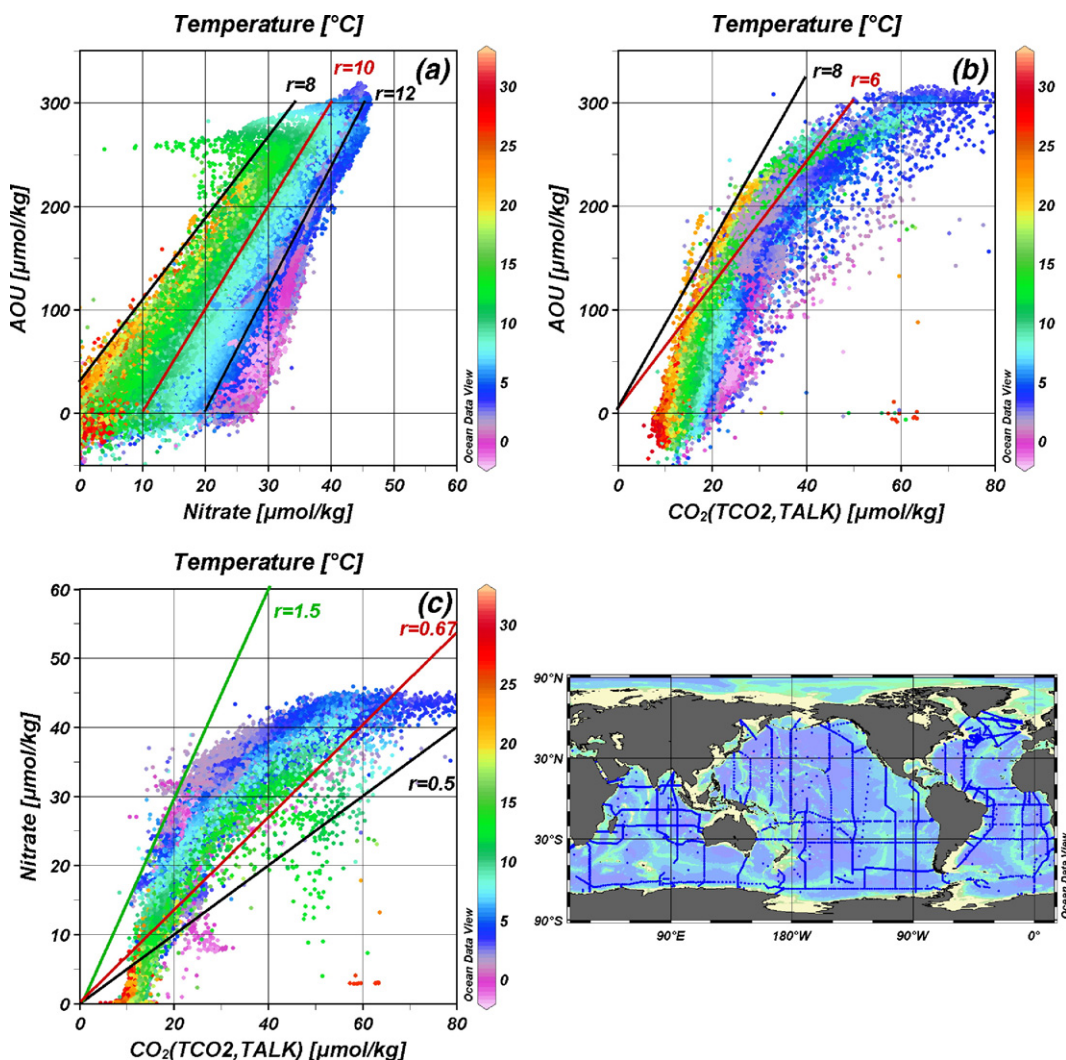


Fig. 1. Scatter plots for (a) AOU vs. [Nitrate], (b) AOU vs. [ $CO_2$ ], and (c) [Nitrate] vs. [ $CO_2$ ] for all stations along all WOCE cruise routes shown in the map.

other hand, the ratio (see Panel (b)) between AOU and [ $CO_2$ ] is not a constant for a constant temperature. It shows a convex pattern. The ratio (at constant temperature) gets smaller when [ $CO_2$ ] gets bigger. But, if an average ratio is needed, the value is 6 for 10 °C isotherm (red line). Some data points indicate negative AOU. That is normal for seawater within the top 100 m or so due to the over saturation of oxygen as a result of photosynthesis. The [ $CO_2$ ] in the euphotic zone is affected by the dissolution of atmospheric  $CO_2$  gas and the utilization by photosynthesis that produces oxygen. Panel (C) shows an envelop of ratio between [nitrate] and [ $CO_2$ ]. A rough estimate of the average is 0.67 (red line).

These ratios of (1) AOU: [nitrate], (2) AOU:[ $CO_2$ ], and (3) [nitrate]: [ $CO_2$ ] have no obvious/direct relation-

ship with the chemical processes within either the nitrogen cycle or carbon cycle of ocean biogeochemistry. But, they are correlated to each other.

The spread of scatter plots (Panels (b) and (c) of Fig. 1) reflects the variation of the chemical and physical properties of seawater and their difference in world oceans. In order to explain the control of those ratios mentioned above, individual station profiles of each parameter are needed.

12 stations were selected based on following criteria: (1) all four parameters (temperature, AOU, [nitrate] and [ $CO_2$ ]) are available, (2) all profiles extend deeper than 2500 m, (3) at least 100 km from the coast, (4) WOCE quality control flags a good observation, (5) represent all three major oceans and their northern and southern



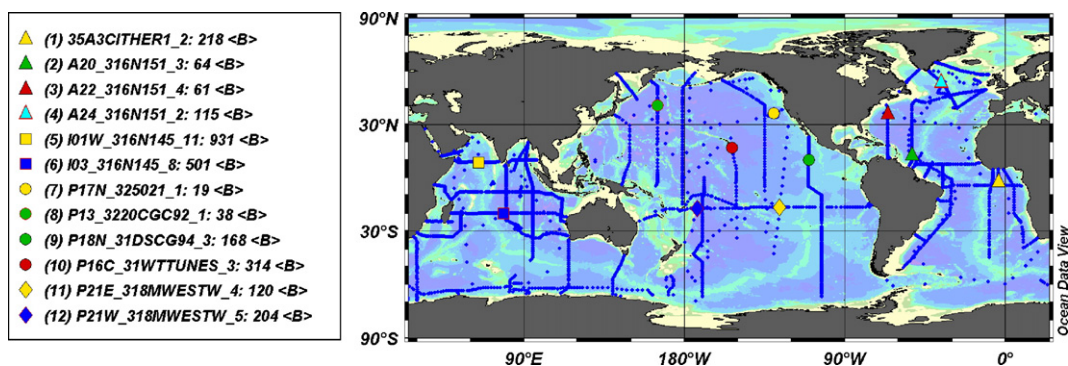


Fig. 2. The WOCE cruise routes and the 12 stations selected for detailed analysis.

basins proportionally to their areas and geography. Fig. 2 shows the locations of those 12 stations. Its legend lists the corresponding WOCE cruise identification and station #s.

Fig. 3 presents the vertical profiles of  $[\text{CO}_2]$  (in Panel (a)) and [nitrate] (in Panel (b)) for the 6 stations in Pacific Ocean. The  $[\text{CO}_2]$  profiles superimpose on the color-coded AOU background scatter plot. These  $[\text{CO}_2]$  profiles present many details that have usually been neglected in books and reports. But, generally, these profiles show a maximum of

$[\text{CO}_2]$  between 300 m and 1500 m depth. All profiles start at an almost constant  $10 \mu\text{M}$  (micro molar) at the surface and end at a value between 30 and  $37 \mu\text{M}$  at 3000 m depth.

The color-coded scatter plot shows vertical bands of AOU spectrum that correlates with  $[\text{CO}_2]$  very well for  $[\text{CO}_2]$  below  $40 \mu\text{M}$ . For those  $[\text{CO}_2]$  maxima greater than  $40 \mu\text{M}$ , the AOU slightly increases with depth.

Panel (b) of Fig. 3 shows smoother [nitrate] profiles compared to  $[\text{CO}_2]$  profiles for the portion of profile above 2000 m. There is also a maximum [nitrate] between 300 m

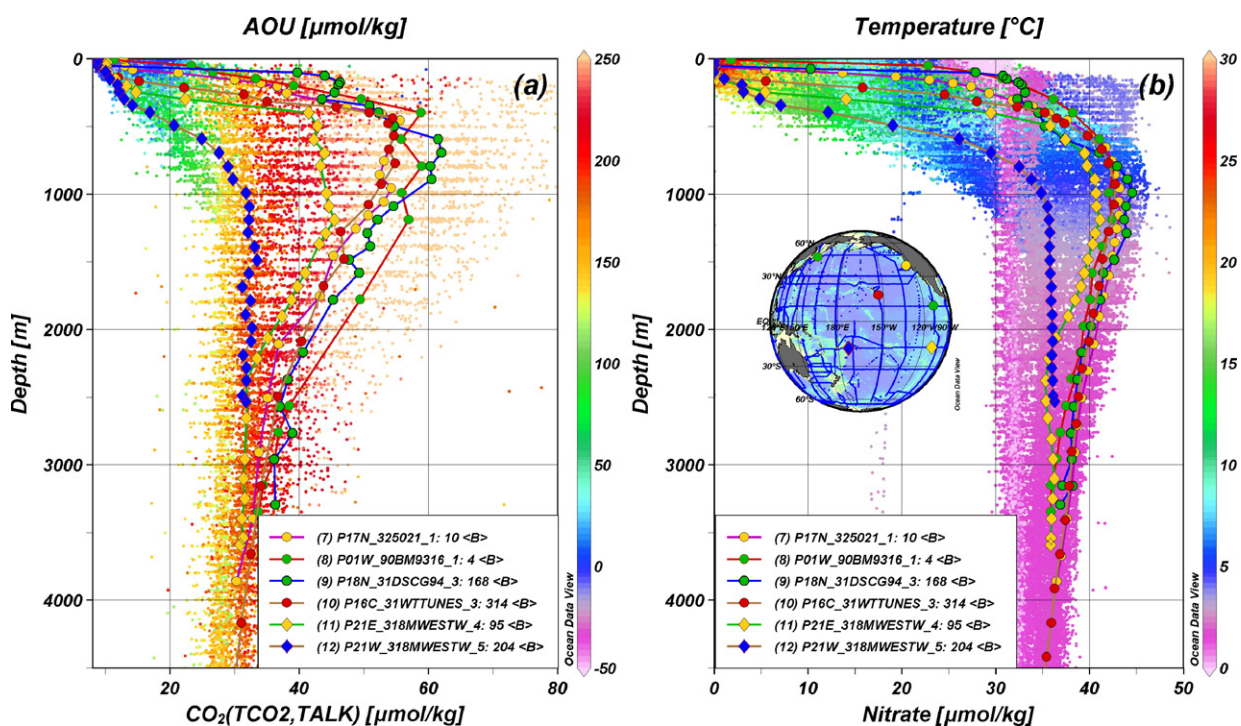


Fig. 3. Scatter plots superimposed with vertical profiles of (a)  $[\text{CO}_2]$  (with AOU), and (b) [nitrate] (with temperature) for the 6 stations in Pacific (shown in the map).

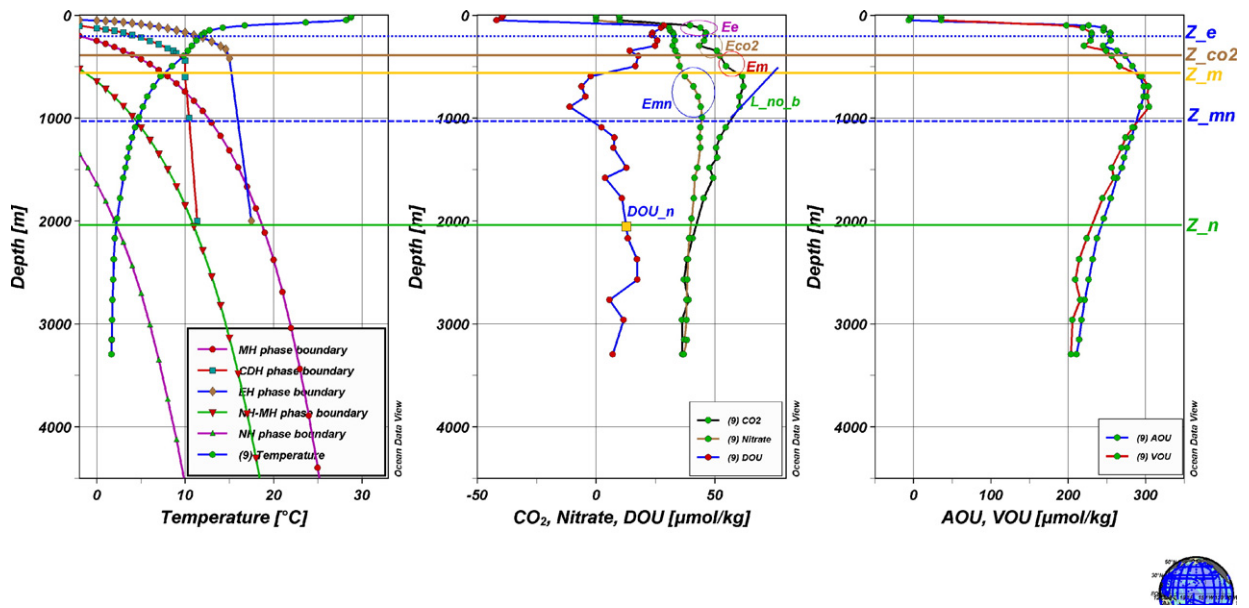


Fig. 4. Vertical profiles for station 9. (a) temperature and gas hydrates equilibria, (b)  $[CO_2]$ ,  $[Nitrate]$  and DOU, and (c) AOU and VOU. See text for details.

and 1500 m depth. But, for each station, the depth for the maximum  $[nitrate]$  is always deeper than that for  $[CO_2]$ .

### 3. Evidences of gas hydrates interfering biogeochemical processes

Fig. 4 shows the linkage between the dissociation of a few kinds of gas hydrate and the biochemical oxidation of the gases in seawater. The profiles of temperature,  $[nitrate]$ ,  $[CO_2]$  and AOU for station 9 are used as examples. Panel (a) shows the seawater temperature profile intersecting the phase boundary curves for hydrates of ethane,  $CO_2$ ,  $CH_4$ , nitrogen–methane mixture, and nitrogen in sequence from shallow water to 2000 m depth. The depths of those intersecting points are marked with horizontal lines across all three panels and labeled at their right ends with  $Z_e$ ,  $Z_{CO_2}$ , etc. The phase boundary for nitrogen–methane mixture is created with data collected in laboratory experiment of the dissociation of hydrate formed with 48% nitrogen and 52% methane (Kang et al., 2001; Seo and Lee, 2001).

Panel (b) shows the set of horizontal lines and the profiles of  $[nitrate]$  and  $[CO_2]$ . Also shown is a profile of a derived parameter – difference in oxygen utilization (DOU). This DOU is obtained by subtracting another derived parameter (virtual oxygen utilization, VOU) from AOU. VOU is computed as:

$$VOU = 2[nitrate] + 3.582[CO_2] \quad (1)$$

The coefficient “2” for  $[nitrate]$  represents the oxygen to nitrate mole ratio in the nitrification. The coefficient “3.582” for  $[CO_2]$  is a combination of 2 and 1.791. This “2” is the oxygen to  $CO_2$  mole ratio in the methane oxidation. The “1.791” is  $120/67$ . These “120” and “67” are the moles of total  $CO_2$  (organic) in seawater vs. the portion that stays as and can be detected as dissolved  $CO_2$ . Out of the 120 mol (Broecker and Peng, 1982), 106 mol are based on Redfield et al. (1963) estimate. Half of the 106 mol (i.e., 53 mol) stay in the form of  $CO_2$  (Sloan, 1998). They and other 14 mol coming from other hydrocarbons add up to 67 mol.

The adequacy of using formula (1) to account for the oxygen utilization in seawater is a subject for future research. Nevertheless, the AOU and VOU profiles in panel (c) of Fig. 4 resemble each other and the difference between is relatively small. It implies that VOU represents the bulk of processes that utilize oxygen in seawater. So, it is used as an approximation to AOU. Refining of VOU in the future should consider other significant chemical processes that involve oxygen in seawater.

The set of horizontal lines intersect each profiles in Panels (b) and (c) of Fig. 4 exactly at where the kinks are. This indicates that those kinks and variations are not meaningless noise due to short-term fluctuations or the accuracy issue. This finding opens a whole new chapter in ocean chemistry. Details are subtle and beyond the scope of this paper and will be discussed in future work.

However, it is very obvious that in an ascending direction (like the ambient environment of a piece of floating MH), the quick decrease of [nitrate] and  $[\text{CO}_2]$  appears in the layer immediately above the level indicating the depth corresponding to the dissociation of one of the gas hydrates. For examples, the decrease of [nitrate] (indicated by Emn) above the  $Z_{\text{mn}}$  level, and the decrease of  $[\text{CO}_2]$  (indicated by Eco2) above the  $Z_{\text{CO}_2}$  level. These decreases of [nitrate] and  $[\text{CO}_2]$  can be explained with the escaping of gas from hydrate and rising as bubbles to a level in the seawater higher or even into the atmosphere.

The nitrogen coming out of the nitrogen hydrate can be fixed then oxidized (by bacteria) into nitrite and finally into nitrate. But, some portion of the nitrite can be converted into nitrous oxide ( $\text{N}_2\text{O}$ ). The solubility of  $\text{N}_2\text{O}$  in seawater is about 0.735 times that of  $\text{CO}_2$ . So, some portion of  $\text{N}_2\text{O}$  will escape into the atmosphere. Since nitrate is not a gas, once it is produced, it stays in the seawater. That explains why [nitrate] profile has a smoother curve. The data from WOCE observation indicate that the [nitrite]:[nitrate] ratio is very small,  $\sim 5\%$ . So, the amount of oxygen depleted by its nitrification can be counted when we know the [nitrate]. Contrary to nitrogen,  $\text{CH}_4$  gets oxidized into  $\text{CO}_2$  that can either dissolve into seawater, or form the  $\text{CO}_2$  hydrate, or escape into the atmosphere through water column. Therefore, the profile for  $[\text{CO}_2]$  is more complicated than that for [nitrate].

VOU represents the amount of oxygen depletion based on the values of the [nitrate] and  $[\text{CO}_2]$  left in seawater only. That is why this author named it “virtual” oxygen utilization. On the other hand, the AOU is influenced by newly dissolved oxygen from the atmosphere and the photosynthesis in the top layer of ocean. Therefore, outside the top layer of ocean, the difference (DOU) between AOU and VOU represents an equivalent amount of the missing  $\text{CO}_2$  after  $\text{CH}_4$  gets oxidized. Panel (b) of Fig. 4 shows a significant (positive) amount of DOU above  $Z_{\text{CO}_2}$  level, reflecting the escaping of  $\text{CO}_2$  gas through seawater. The DOU profile above the  $Z_e$  level should be ignored because of the absorption of atmospheric  $\text{CO}_2$  by seawater and the photosynthesis process.

#### 4. Discussion

The results of these analyses led to following observations. There is an internal heat generator within the body of oceans. The chemical energy (in the form of heat at a rate of  $\sim 195$  Kcal/mol of  $\text{CH}_4$ ) released from step-by-step oxidation of  $\text{CH}_4$  by oceanic organisms

might accumulate to an amount such that it can significantly influence ocean thermodynamics. The rate of heat-generation can vary from time to time and place to place. This can lead to the observed differential ocean warming at intermediate depth ( $\sim 450$  m) as reported by Levitus et al. (2001).

The oxidation of  $\text{CH}_4$  into  $\text{CO}_2$  within seawater might be the cause of the relatively smaller atmospheric concentration of  $\text{CH}_4$  compared to that of  $\text{CO}_2$ . Because  $\text{CO}_2$  is less powerful as a greenhouse gas than  $\text{CH}_4$  is, this sets a brake on the atmospheric greenhouse effect. Recent increase of atmospheric  $\text{CH}_4$  concentration may imply a change of ocean dynamics, chemistry and biology.

#### 5. Conclusions

Various hydrates of natural gases may form and float in seawater. This may account for a much greater amount of hydrate. If a technology is available to collect those floating tiny gas hydrates for energy production, then that may provide a tremendous amount of energy. Their formation and dissociation may interfere the biochemical reactions and influence chemical properties (like pH value) and physical properties (like density).

The formation and dissociation of hydrate alter the heat content of seawater at various depths. The buoyancy associated with hydrates and seawater may significantly alter the stratification of seawater. Hydrates can be seen as the “snow” within the sea. Careful analysis of ocean biogeochemical data may help locate the site of possible MH deposits that might be undetected otherwise.

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#### References

- Broecker, W.S., Peng, T.H., 1982. Tracers in the Sea. Eldigio Press, Palisades, NY.
- Dickson, A.G., Goyet, C., 1994. Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water. Version 2, US. DOE, SGRP-89-7A.
- Fisher, C.R., MacDonald, I.R., Sassen, R., Young, C.M., Macko, S.A., Hourdez, S., Carney, R.S., Joye, S., McMullin, E., 2000. Methane Ice Worm: *Hesiocaeca methanicola* colonizing fossil fuel reserves. *Naturwissenschaften* 87, 184–187.
- Kang, S.-P., Lee, H., Lee, C.-S., Sung, W.-M., 2001. Hydrate phase equilibria of the guest mixtures containing  $\text{CO}_2$ ,  $\text{N}_2$  and tetrahydrofuran. *Fluid Phase Equilibria* 185, 101.

- Levitus, S., Antonov, J.I., Wang, J., Delworth, T.L., Dixon, K.W., Broccoli, A.J., 2001. Anthropogenic warming of Earth's climate system. *Science* 292, 267–270.
- Redfield, A.C., Ketchum, B.H., Richards, F.A., 1963. The influence of organisms on the composition of seawater. In: Hill, M.N. (Ed.), *The Sea*, vol. 2. Wiley Interscience, New York, pp. 26–79.
- Reeburgh, W.S., Whalen, S.C., Alperin, M.J., 1993. The role of microbially-mediated oxidation in the global CH<sub>4</sub> budget. In: Murrell, J.C., Kelley, D.P. (Eds.), *Microbiology of C<sub>1</sub> Compounds*. Intercept, Andover, U.K., pp. 1–14.
- Schlitzer, R., 2004. Ocean Data View. <http://www.awi-bremerhaven.de/GEO/ODV> 2004.
- Seo, Y.-T., Lee, H., 2001. Multiple phase equilibria of the ternary carbon dioxide, methane and water mixtures. *J. Phys. Chem. B* 105, 10084.
- Sloan, E.D., 1998. *Clathrate Hydrates of Natural Gases*, 2nd edition. Marcel Dekker, New York.
- Stenesh, J., 1998. *Biochemistry*. Plenum Press, New York ISBN 0-306-45732-6.